Journal of Molecular Liquids 256 (2018) 58–66

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

New aspects in the thermochemistry of solid-liquid phase transitions of organic non-electrolytes

Mikhail I. Yagofarov, Ruslan N. Nagrimanov, Boris N. Solomonov *

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia

ARTICLE INFO

Article history:
Received 31 October 2017
Received in revised form 28 December 2017
Accepted 20 January 2018
Available online 13 February 2018

Keywords:
Fusion enthalpy
Solution enthalpy
Sublimation enthalpy
Organic non-electrolytes

ABSTRACT

Thermochemistry of solid-liquid phase transitions plays an important role in solidification studies of polymers, metals, inorganic salts, and low-molecular organic compounds. Enthalpy of fusion is a source of information about intermolecular interactions in materials, crystallinity, mixtures phase diagrams shape, heat transfer in the solidification interval.

The present paper is devoted to relationship between the fusion enthalpies of aromatic compounds at the melting temperature and the solution enthalpies in benzene at 298.15 K. Sublimation and vaporization thermochemistry are used as an additional source of information about the latter relationship. Depending on the magnitude of deviation between the solution enthalpies in benzene at 298.15 K and fusion enthalpies at the melting temperature, aromatic compounds are conventionally divided into three groups. For a large number of aromatic compounds not capable of self-association the equality between the fusion enthalpies at the melting temperature and the solution enthalpies in benzene at 298.15 K is established. For self-associated aromatic compounds the solution enthalpy in benzene at 298.15 K exceeds the fusion enthalpy at the melting temperature, and insertion of a substituent not forming inter- and intramolecular hydrogen bonds does not affect the difference between the solution and fusion enthalpies. The enthalpies of solution in benzene at 298.15 K of several aromatic compounds not capable of self-association appear to be visibly less than the fusion enthalpies at the melting temperature. The reasons of different relationships between the fusion and solution enthalpies are analyzed using Kirchhoff's law for the fusion enthalpy.

1. Introduction

Calorimetry has been used extensively in materials science since the 19th century. Nowadays it is necessary in both fundamental and applied investigations of metals and alloys, polymers, composites, inorganic salts, ceramics and glasses, organic low-molecular compounds.

One of the key quantities obtained using calorimetry is the enthalpy of fusion. The fusion enthalpies of pure compounds are commonly used for prediction and analysis of solid-liquid equilibrium phase diagrams shapes, including studies of mixtures of metals [1], inorganic salts [2], organic compounds [3,4]. In the case of low-molecular organic compounds, especially biologically active substances, the solubilities in water, common organic solvents, and mixtures are frequently predicted with the use of the fusion enthalpies [5–11]. Calorimetric methods involving latent heat of fusion measurement find application in investigation on polymorphic modifications [12–14]. The fusion enthalpy value is important for the modeling of heat transfer during solidification process in metals [15–19] and polymers [20]. One of the widest applications of fusion enthalpy measurements is a determination of a degree of crystallinity in semi-crystalline polymers [21–29] and blends, e. g. poly (3-hydroxybutyrate) – poly(ethylene glycol) [30], hydroxypropyl cellulose – polyvinyl alcohol [27], hydroxypropyl lignin – polyvinyl alcohol [31].

Many techniques exist which allow determining fusion enthalpy at the melting temperature ($\Delta^{l}_{cr}H^{A_i}(T_m)$) with varying accuracy: dynamic methods, such as differential scanning calorimetry [32] and its modifications (temperature modulated differential scanning calorimetry [33], fast scanning calorimetry [29], etc. [34]); adiabatic calorimetry [34–37]; mixtures phase-change calorimetry (e.g. ice calorimeter [38]); drop calorimetry [39,40]; levitation techniques [41]; freezing point method [42]; derivation from sublimation and vaporization enthalpies [43]. Several reviews are available on calorimetric methods of measurement of solid-liquid phase change enthalpies [34,44–46].

Apart from correct device handling during an experiment, measurement accuracy strongly depends on the quality of specimen preparation and its thermal stability. Presence of impurities, high-temperature chemical processes in the sample can drastically affect fusion enthalpy magnitude.

* Corresponding author.
E-mail address: boris.solomonov@kpfu.ru (B.N. Solomonov).

https://doi.org/10.1016/j.molliq.2018.01.114
0167-7322/